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TECHNICAL NOTE 3787

HEAT-CAPACITY MEASUREMENTS OF TITANIUM AND OF A HYDRIDE
OF TITANIUM FOR TEMPERATURES FROM 4° TO 15° K
INCLUDING A DETAILED DESCRIPTION OF A SPECIAL
ADIABATIC SPECIFIC-HEAT CALORIMETER

By M. H. Aven, R. S. Craig, and W. E. Wallace

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SUMMARY

An adiabatic specific-heat calorimeter bridging the interval between 4° and 15° K temperatures is described. The instrument uses a constant-volume helium gas thermometer as the working thermometer. The sample is placed directly in the gas-thermometer bulb which thus acts as the sample container. A semiautomatic direct-reading manometer is used for rapid pressure measurements.

Heat-capacity measurements, employing this calorimeter, were made on a sample of 8.0289 gram atoms of high-purity titanium covering the range of 4° to 15° K. Up to about 13° K the data can be represented by the equation $C = 3.38 \times 10^{-3}T + 2.596 \times 10^{-5}T^3$ where C is heat capacity in joules per gram atom degree and T is absolute temperature. The average difference between the measured values and those computed from the equation is 1.57 percent.

Heat-capacity measurements were also made on a sample consisting of 7.558 gram atoms of titanium and 2.563 gram atoms of hydrogen. Up to 13° K the heat capacity of the sample was found to obey the equation $C = 0.0242T + 2.294 \times 10^{-4}T^3$ joules per degree, with the average difference between measured and calculated values of C equal to 0.56 percent. The interpretation of the results is discussed on the basis of the assumption that the sample consists of two phases, one of pure titanium Ti and the other of titanium and hydrogen TiH.

INTRODUCTION

In connection with a research program at the University of Pittsburgh dealing with the energies of alloy systems, an adiabatic specific-heat

calorimeter has been developed for use in the temperature range of 4° to 15° K. Several features distinguish this calorimeter from the more conventional instruments commonly used in this range. These are (1) the use of a constant-volume gas thermometer as the working thermometer, rather than the more common semiconducting resistance elements; (2) the inclusion of the sample directly in the chamber of the gas thermometer to assure thermal contact between the sample and the gas; (3) a cooling method which employs a Monel tube to transfer the cooling agent to the sample container, thus avoiding the use of helium exchange gas in the vacuum jacket; and (4) the use of an adiabatic shield employing a special thermocouple to indicate the temperature difference between the sample and its environment. Because of its distinctiveness, this instrument is described herein in detail.

The principle aim of this research as set forth initially was to measure, using the special calorimeter, the heat capacities of pure titanium Ti and of titanium containing various amounts of dissolved hydrogen TiH between 4° and 15° K. Measurements of the heat capacity of metals at temperatures near absolute zero yield information concerning the heat capacity of the conduction electrons, which is in turn related to the density of the electronic energy states in the metal. If the hydrogen exists in the metal as protons, and if the electrons from the hydrogen atoms enter the conduction band of the metal, it would be expected that the degree to which the available energy states in the conduction band are filled could be altered by varying the quantity of hydrogen dissolved in the metal. The results of these experiments would permit construction of a portion of the curve representing the variation of the density of states as a function of energy.

When these experiments were started, the best available information concerning the crystal structure of the titanium hydrides at room temperature was given in a publication by Hägg (ref. 1). Hägg indicated that titanium would dissolve up to 33 atomic percent of hydrogen while still retaining the hexagonal crystal habit of pure titanium. The lattice parameters showed a steady increase as the hydrogen content became larger, but no second phase appeared until the above-mentioned concentration limit was exceeded. It appeared then that no fundamental difficulty stood in the way of carrying through the initial experimental plan. However, a recent publication (ref. 2) by a research group covering work done at the Battelle Memorial Institute describes experiments, the results of which are quite at variance with Hägg's findings. These workers found that hydrogen cannot be retained by α titanium at low temperatures, but that upon cooling to room temperature a face-centered cubic structure appears. This new phase is known as the γ phase and appears to be identical with Hägg's β phase. The reasons for the disagreement between Hägg and the more recent workers are not clear. One reason for the lack of clarity is that Hägg did not completely describe the details of his treatment of the sample. The possibility is suggested

that differences in sample purity might affect the retention of hydrogen. Extremely high purity titanium has become available only since Hagg's work.

Experience gained in the present research bears out the findings (ref. 2) of Lenning, Craighead, and Jaffee of Battelle. Powder X-ray photographs of the sample used herein show evidence of two phases even at hydrogen concentrations below 10 atomic percent. Thus, the initial objective of preparing homogeneous samples of varying hydrogen content could not be realized. Two possible courses of procedure remained: (1) Heat-capacity measurements could be performed on samples containing two phases, titanium and the γ phase (hydride), realizing that complete and unambiguous interpretation of the results may have to be postponed until more precise information about the phase diagram of the TiH system at room temperature becomes available, or (2) sufficient hydrogen could be added to the sample to convert it completely to the γ phase. For this second procedure the hydrogen content would be varied between approximately 50 and 66 atomic percent in a homogeneous system having a face-centered cubic structure. In a sense, this second procedure would be disadvantageous in that any conclusions concerning the density of states which might be deduced from the data would not be applicable to hexagonal titanium. Perhaps a more practical objection arises from the fact that the introduction of sufficient hydrogen to convert the sample completely to the γ phase produces a very brittle structure with many rifts and cracks, having in all probability a relatively high surface area. Since measurements on samples of this sort are subject to the uncertainties introduced by helium adsorption, procedure (2) was ruled out. Accordingly, a sample was prepared which consisted of 7.556 gram atoms of titanium and 2.563 gram atoms of hydrogen and which was a mixture of the α and γ phases. Thus, this report describes the heat-capacity measurements on this alloy and on a sample of pure titanium.

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SYMBOLS

A	cross-sectional area of tube
C	heat capacity
C_e	electron contribution to heat capacity
C_n	effective heat capacity of helium in thermometer bulb

C_v	heat capacity at constant volume
C_{vib}	vibrational heat capacity
dl	differential of length
dq	change in quantity of heat
dS	change of entropy
$f(T,P)$	factor accounting for gas imperfections
$g(e')$	density of states at Fermi level
k	Boltzmann's constant
n	number of moles of material
n_0	total number of moles of gas in system
n_1	number of moles of helium in thermometer bulb
P	pressure
R	gas constant
T	absolute temperature
T_i	any term in series T_n
T_n	indicates series of temperatures
V	volume
V_1	volume of thermometer bulb
V_i	any term in series V_n
V_n	indicates series of volumes
v	molar volume
γ	temperature coefficient of electronic specific heat
θ	Debye's characteristic temperature
ρ	density

ADIABATIC SPECIFIC-HEAT CALORIMETER FOR
TEMPERATURE RANGE OF 4° TO 15° K

General Description

Most of the previously reported calorimetric measurements in the range below 10° K have been carried out by the use of resistance thermometers, carbon and other semiconductors being commonly used (refs. 3 and 4). While these thermometers have high sensitivity, all of them must be calibrated against some standard thermometric device, usually a helium vapor-pressure thermometer. Moreover, the conversion of resistance measurements into temperatures is not always unambiguous. Above the critical temperature of helium one has either to interpolate between the highest obtainable point on the liquid-helium vapor-pressure scale (ref. 3) or to calibrate the resistance thermometer against a helium gas thermometer (ref. 5).

The use of the gas thermometer as the working thermometer avoids this problem of calibration. The successful application of the gas thermometer in this capacity requires accurate determination of the dead-space volumes before assembly and rigorous control of the temperature distribution along the thermometer tube. A method of making rapid and accurate pressure measurements is also essential, and a semiautomatic direct-reading manometer has been constructed which renders the measurement of pressure both convenient and rapid.

The ways in which the special features of the calorimeter are incorporated in the apparatus will be brought out in the following sections where the essential components are briefly described. These features, which have already been mentioned, are (1) the use of a constant-volume gas thermometer as the working thermometer, rather than the more common semiconducting resistance elements; (2) the inclusion of the sample directly in the chamber of the gas thermometer to assure thermal contact between the sample and the gas; (3) a cooling method which employs a Monel tube to transfer the cooling agent to the sample container, thus avoiding the use of helium exchange gas in the vacuum jacket; and (4) the use of an adiabatic shield employing a special thermocouple to indicate the temperature difference between the sample and its environment.

Cryostat Assembly

A schematic diagram of the cryostat assembly is shown in figure 1. Liquid helium is contained in the glass Dewar vessel (1.12), which is supported by the brass cylinder (1.8). The space above the liquid helium leads to the tube (1.3), through which it is possible to evacuate the

liquid-helium chamber. The Dewar is surrounded by a protective envelope of liquid nitrogen contained in the glass Dewar vessel (1.5).

The central portion of the apparatus extending downward into the liquid-helium Dewar ends with the vacuum jacket (1.15) which houses the sample container (1.18) and the adiabatic shield (1.17). The vacuum jacket can be opened and closed at the soft-solder joint (1.16). These components are ultimately supported by the heavy brass plate (1.4) connected to a steel frame upon which is fastened most of the auxiliary equipment such as manometers, gas-measuring bulbs, diffusion pumps, and electronic equipment. The vacuum jacket is suspended from the Monel tube (1.13) which has a wall thickness of 0.008 inch. The jacket is evacuated through the tube (1.2) near the top of the apparatus. The vacuum in this enclosure is monitored by a helium mass-spectrograph leak detector, vacuums of the order of 10^{-9} millimeters of mercury (Hg) being maintained during the operation of the calorimeter (ref. 6).

Inside the Monel tube (1.13) is a coaxial Monel tube (1.14) extending down to the level marked (d). This tube is open at the top and serves as a reentrant well to hold liquid nitrogen. The well shields the interior of the vacuum jacket from radiation from above and maintains the thermometer tube (1.6) at a constant temperature. The reentrant well is supported by the copper ring (1.10) which is soldered to the well and to which the upper and the lower sections of the Monel tube (1.13) are soldered. A series of vertical holes in the ring provide a free path for evacuation through the annular space. The copper disk (1.11) extends outward from the ring. Being in thermal contact with the nitrogen well, the disk forms a radiation shield protecting the liquid helium in the Dewar. The Sylphon bellows (1.1) and (1.7), as well as the zigzag bends in the thermometer tube (1.6), serve to eliminate strains caused by differential thermal expansion of parallel components.

Sample Container

The sample container, shown in figure 2, is fabricated from copper and divided into two chambers. The upper chamber (2.1) serves as a receptacle into which liquid helium drops during the cooling procedure and can be used as a vapor-pressure thermometer. The lower chamber (2.2) contains the sample and serves as the gas-thermometer bulb. The sample container is provided with two bottoms of the same material and the same weight. Bottom (2.3) is used for the measurement of the heat capacity of the empty sample container. When soldered in place, it provides a volume of about 25 cubic centimeters for the helium gas. Bottom (2.4) is used when the sample is introduced into the sample container. The volume available to the gas is now adjusted to 25 cubic centimeters by an appropriate choice of the amount of the material under investigation. Thus, using approximately equal amounts of helium gas for each series of determinations, uncertainties in the specific heat of helium are

largely canceled out. The bottoms are soft soldered to the sample container at the joint (2.5). A winding of No. 36 Advance wire on the exterior of the sample container serves as a heater.

Adiabatic Shield

The adiabatic shield (fig. 2) consists of a solid copper block (2.7) wound with a heater of No. 36 Advance wire. Underneath this winding is a helical groove having a length of about 15 inches. The current and the potential leads to the sample-container heater are cemented into this groove to insure good thermal contact with the shield. After the sample container is fastened in place, the copper cylinder (2.8) enclosing the sides of the sample contained is soldered to the bottom of the shield block. The temperature difference between the sample container and the shield is indicated by a cobalt-gold to silver-gold differential thermocouple¹ and read on a Leeds and Northrup type H. S. galvanometer. All wires coming from the adiabatic shield are thermally bonded to the top of the vacuum jacket before passing up through the annular space between the supporting tubes (1.13) and the well (1.14) (see fig. 1) and out of the vacuum system through an Apiezon wax seal at room temperature.

Manometer

Figure 3 is a schematic diagram of the manometer system. The center column is a glass tube 2.5 centimeters in diameter and somewhat more than 76 centimeters long, the upper end of which is connected to a diffusion pump through the tube (3.17). The other arm (3.14) is connected to the thermometer tube issuing from the sample container. The lower ends of these tubes are sealed into steel cups with o-rings. Mercury travels between the cups through the connections of welded steel tubing (3.12). The difference between the mercury levels in tubes (3.14) and (3.15) gives the absolute pressure in the sample-container bulb.

Since the space above the mercury in tube (3.14) is a portion of the constant-volume gas thermometer system, the quantity of mercury in the manometer must be continuously adjusted so that the level in the tube (3.14) is constant. This level is defined by the point of a steel needle fixed in the axis of the tube. The automatic adjustment of the mercury level is accomplished by altering the pressure of air above the

¹The wire for the thermocouple was obtained through the courtesy of Dr. W. DeSorbo of the General Electric Research Laboratories, Schenectady, N. Y. The compositions were 96.8 percent gold with 3.2 percent cobalt and 99.615 percent silver with 0.325 percent gold.

mercury surface in tube (3.11). The magnitude of the pressure in this tube is determined by the balance between the rate at which air is pumped out through the throttle valve (3.10) and the rate at which it leaks in through the porous glass disk (3.9). Only air passes readily through this disk, mercury being held back unless considerable pressure is applied. Thus, when mercury, which fills the U-tube below the disk (3.9), rises to cover the surface of the disk, the air leak is stopped. The slight motion of the mercury surface at the disk (3.9) is caused by the solenoid magnet (3.8) which acts on the small iron weight (3.7) resting upon the mercury surface. Energizing the solenoid lifts the weight and causes the level in the U-tube to fall, exposing the porous disk (3.9). Air then leaks into tube (3.11) from tube (3.5). The pressure in tube (3.5) is kept at all times about 30 millimeters Hg higher than that in tube (3.11) by regulating the rate at which air enters (3.5) from the outside by means of another porous-disk-solenoid combination, (3.4) and (3.3).

The power to the solenoid magnet (3.8) is delivered by the plate circuit of a 2D21 tube, the grid of which receives a negative bias when mercury in tube (3.14) touches the needle above it. Similarly, contact between the probe (3.1) and the mercury in tube (3.2) controls the power to the solenoid (3.3). The ballast (3.6) serves to cut down the amplitude of oscillations of the mercury in tube (3.14). The frequency of the oscillations is about 1 per second, and the amplitude is less than 0.02 millimeter. Rapid adjustments of the mercury level can be carried out manually with a cylinder-and-piston arrangement connected to the manometer at (3.13).

Along the axis of the tube (3.15) and entering the tube through a vacuum-tight o-ring seal (3.18) is the probe (3.16), the lower end of which bears a steel needle. The upper end of the probe is connected to the micrometer screw (3.21) which is coupled to a Durant counter by means of the tube (3.20) and the nut (3.22). Vertical motion of the probe is brought about by the rotation of the nut. For relatively rapid changes the nut is rotated by a reversible electric motor, while fine adjustments can be performed manually. A pressure reading is taken when the needle at the end of the probe touches the mercury in tube (3.15). This is indicated by a flash of a neon signal lamp actuated through a thyatron circuit. The pressure is read directly in millimeters on the Durant counter, while fractional parts of a millimeter are read on the graduated ring (3.19). The whole manometer structure is enclosed in a cabinet thermostated to $\pm 0.02^{\circ}$ C. The manometer has been found to reproduce pressure readings to ± 0.02 millimeter of Hg.

Operation of Calorimeter

The calorimeter is operated as follows: The cooling of the sample container is started with liquid nitrogen in both Dewar vessels and

nitrogen gas at a pressure of about 150 millimeters of Hg inside the vacuum jacket. When the system has cooled to about 80° K, the nitrogen gas is pumped out of the vacuum jacket and the liquid nitrogen in the inner Dewar is replaced by liquid helium.

By means of the two concentric Monel tubes, (1.9) and (2.6), passing through liquid helium and leading into the upper chamber of the sample container, cold helium gas is circulated through the adiabatic shield and the upper chamber of the sample container. As these become colder, some liquid helium starts dripping down through the shield into the sample container where it reevaporates, absorbing heat. Refluxing continues until the temperature of the sample container and contents falls sufficiently low for liquid helium to collect in the chamber. When a few cubic centimeters of liquid have collected, the pressure on the liquid is reduced to slightly less than atmospheric, whereupon the temperature adjusts itself accordingly. During the cooling procedure helium gas has been drawn into the gas-thermometer system from a calibrated and thermostated glass bulb. The quantity of gas is chosen to give a pressure of about 180 millimeters of Hg at 4° K. At this point the vapor pressure of the liquid helium in the liquefaction chamber and of the helium-gas pressure in the lower chamber of the sample container are measured simultaneously. The liquid is then removed from the upper chamber by pumping it through the tube (1.9) (fig. 1).

From this point the measurements proceed by the usual method employed in adiabatic specific-heat calorimetry. A series of measurements is made to ascertain that the temperature of the sample is constant, as evidenced by constant-pressure readings on the manometer. A measured quantity of heat is introduced into the sample electrically, and observations of temperature are again made, followed by another heating period, and so on. The ratio of energy input to the difference of the temperatures before and after each heating period gives the heat capacity. During the heating as well as the rating periods the temperature of the adiabatic shield is kept as close to that of the sample container as possible.

Electrical measurements are made with a White double potentiometer in conjunction with a Leeds and Northrup type H. S. galvanometer. The optical system is such that the sensitivity is approximately 0.04 micro-volt per millimeter scale deflection.

Conversion of pressure to temperature.— Pressure is related to temperature as follows. The temperature of a constant-volume gas thermometer is given by

$$T = \frac{PV_1}{R \left(n_0 - \frac{P}{R} \sum \frac{V_1}{T_1} \right) f(T, P)}$$

where P is the pressure, V_1 is the volume of the thermometer bulb, n_0 is the total number of moles of gas in the system, R is the gas constant, V_i is any term in the series V_n , T_i is any term in the series T_n , and $f(T,P)$ is a factor accounting for gas imperfections. The dead space is divided into sections $V_2, V_3, \dots V_n$ corresponding to regions of constant temperature or to regions for which the thermal gradient is known. The temperatures (or, for the regions of thermal gradient, the "effective" temperatures) corresponding to these volumes are indicated by the terms $T_2, T_3, \dots T_n$. The effective temperatures for the gradients should in principle be determined by integrating the following expression between appropriate limits:

$$\frac{V_i}{T_i} = \int \frac{A \, dl}{T}$$

The cross-sectional area of the tube is represented by A , the differential of length is dl , and T is the temperature at any point along the tube. In the relatively small temperature ranges involved, the variation of the thermal conductivity of Monel with temperature can be represented by a linear equation. This makes it possible to obtain a steady-state expression for the variation of temperature along the tube which renders the above equation integrable. This method of calculating the effective temperature gave results which differed significantly from the arithmetic average only for the difference between the temperature of the helium bath and the temperature of the nitrogen well.

The number of moles of gas in the thermometer system n_0 is determined directly by measuring the pressure and volume of the gas as it is introduced into the thermometer system from a thermostated glass bulb. The dead-space volumes, V_2 to V_7 in the present case, were determined by measuring the volumes of the different sections of the thermometer tube before assembly. The temperatures of the dead spaces are represented as follows: T_2 is the average of the temperatures at the points (a) and (b) in figure 1, that is, the average between the temperature of the sample container and the liquid-helium bath; T_3 is the temperature of the liquid-helium bath; T_4 is the effective temperature between the liquid helium at the point (c) and liquid nitrogen at the point (d); T_5 is the temperature of the liquid nitrogen in the well, indicated by a copper constantan thermocouple; T_6 is the average between the point (e) at liquid nitrogen temperature and the point (f) near room temperature; and T_7 is the temperature of the manometer cabinet. The function $f(T,P)$ is obtained from the equation of state for helium with

three virial coefficients. The volume of the thermometer bulb V_1 is determined by employing the results of measurements described in the section entitled "Operation of Calorimeter." It was stated in that section that after a few cubic centimeters of liquid helium have collected in the upper chamber of the sample container, simultaneous measurements are taken of the helium vapor pressure in this chamber and of the helium gas pressure in the lower chamber. The temperature of the sample container can be computed from the helium vapor pressure. Since T and P are known, V_1 can then be calculated from the equation for T .

Calculation of heat capacity.- The heat capacity of the sample at a particular temperature is obtained by subtracting the heat capacity of the sample container and of the helium gas in the sample container from the total measured heat capacity. Below 5° K and at the pressures employed in these experiments the departure of helium from ideal behavior causes the heat capacity to be slightly lower than the ideal value. Corrections were made employing the virial coefficient data collected by Keesom (ref. 7). It should be noted that the quantity of helium in the thermometer chamber decreases continuously as the temperature of the chamber is raised during the heating period. This variation in the number of moles of gas must be taken into account in computing the effective heat capacity of helium. Details of this calculation are presented in the appendix.

Limitation of equipment.- The precision of the heat-capacity measurements is discussed in detail in the sections where the results of measurements on titanium and on a hydride of titanium are presented.

The authors are aware of the possibility of helium being adsorbed upon the sample in experiments of this kind. An appreciable amount of adsorbed helium would introduce errors in thermometry and would also contribute to the effective heat capacity of the system because of desorption on heating. The samples used in these investigations were of low surface area (as measured by krypton adsorption isotherms) and the amount of adsorbed helium is believed to be negligible. It is clear, however, that attempts to use finely divided materials in this calorimeter would lead to difficulties.

HEAT CAPACITY OF TITANIUM

Experimental Procedure

The experiments were conducted on a mass of 384.390 grams (8.0289 gram atoms) of high-purity titanium bar which was used in measuring the atomic heat of titanium. The material was manufactured by the Foote Mineral

Company by the Van Arkel process (thermal decomposition of titanium tetraiodide). Spectrographic spot checks made by the company showed that the material manufactured by them was generally of 99.95 to 99.99 percent purity, a typical analysis, given in percent, being: silicon, 0.005; aluminum, 0.0001; magnesium, 0.0002; manganese, 0.001; chromium, 0.0005; tin, 0.0001; iron, 0.0003; nickel, 0.0001; calcium, 0.0005; copper, 0.001; carbon, 0.001; oxygen, 0.002; and nitrogen, 0.002.

The titanium, received in two 19-inch bars about 0.375 inch in diameter, was sawed into pieces approximately 2.8 inches long. The material was sealed in a Pyrex flask which was then evacuated and flushed with high-purity helium gas three times. After annealing for 3 hours at 500° C in helium atmosphere, the titanium was cooled slowly to room temperature and sealed in the calorimeter.

The heat-capacity determination was made in the following sequence: 16 measurements between 5.686° and 15.555° K, 5 measurements ranging from 3.946° to 5.867° K, 5 measurements from 11.691° to 14.287° K, and 7 measurements between 6.348° and 10.243° K. After the first 26 measurements the sample container was evacuated and a new quantity n_0 of helium gas was measured out and introduced into the gas-thermometer system. The volume of the thermometer bulb V_1 was determined at five different temperatures, three times with the first filling and two times with the second. There was no systematic deviation in V_1 or in the heat capacity with different fillings.

Results

The vibrational heat capacity C_{vib} of a metal at low temperatures is, according to the Debye theory, represented by the expression

$$C_{vib} = 1943.7 \left(\frac{T}{\theta} \right)^3 = \beta T^3 \frac{\text{joules}}{\text{g atom deg}}$$

where θ is Debye's characteristic temperature and T is the absolute temperature. The contribution of the electrons to the heat capacity per gram atom of metal is given, according to the free-electron theory, by the expression

$$C_e = \frac{2}{3} \pi^2 k^2 g(e') T = \gamma T$$

where k is Boltzmann's constant, $g(e')$ is the density of states at the Fermi level, γ is the temperature coefficient of the electronic specific heat, and T is the absolute temperature. The total heat capacity is the sum of these two expressions and is given by

$$C = \gamma T + \beta T^3$$

This may be written in the more convenient form

$$\frac{C}{T} = \gamma + \beta T^2$$

Thus, according to theory, a plot of C/T versus T^2 should give a straight line, the intercept of which is γ , the temperature coefficient of the electronic specific heat, and the slope of which is related to the Debye θ . The experimental points for titanium plotted in this manner fall close to a straight line up to 13° K. Above this temperature an upward curvature becomes noticeable. The plot is shown in figure 4. A least-squares treatment gave the following equation for the "best" straight line through the experimental points below 13° K:

$$\frac{C}{T} = 3.38 \times 10^{-3} + 2.596 \times 10^{-5} T^2 \frac{\text{joules}}{\text{g atom deg}^2}$$

From this equation γ is seen to be 3.38×10^{-3} . The characteristic temperature θ is found to be 421.5° K. The original data are presented in table I.

Precision

The precision of the measurements is graphically represented in figure 5 where the deviation of the measured values of the heat capacity from the values computed from the least-squares equation is plotted as a function of temperature. For 26 points below 13° K the average deviation is 1.57 percent.

Discussion

In this discussion the values of γ and θ obtained from the heat-capacity measurements of pure titanium are compared with those of Estermann, Goldman, and Friedberg (ref. 4) who made measurements on a sample of titanium from approximately 2° to 4° K. They found that

$\gamma = 3.35 \times 10^{-3} \frac{\text{joules}}{\text{g atom deg}}$ which is in excellent agreement with the results presented herein. Their value for θ , however, is 280° K , which is considerably lower than the value found in this research. Kothen and Johnston (ref. 8) report a value of 360° K for θ which is based upon measurements extending down only to about 15° K .

It is difficult to indicate with certainty the cause of the discrepancy between the value of θ obtained in the present investigation and that reported in reference 4. The purity of the samples used in reference 4 was stated to be approximately 99 percent. It is quite possible that small amounts of impurities may profoundly affect the elastic properties of the metal and thus reduce θ without sensibly altering the population of the energy levels.

HEAT CAPACITY OF A HYDRIDE OF TITANIUM

Experimental Procedure

The hydride sample was prepared according to the following procedure: Sticks of high-purity titanium bar were placed in a furnace in a Pyrex tube. The tube was connected to an external system whereby the sample tube could be evacuated and a known amount of hydrogen metered in volumetrically. The titanium was protected from possible contamination from the glass by lining the Pyrex tube with platinum foil. The hydrogen was purified by passing it through a charcoal trap under high pressure at the temperature of liquid nitrogen.

The hydrogen was taken up rapidly by the titanium at 500° to 550° C after which the sample was allowed to remain sealed in the furnace for about 20 hours. It was then cooled to about 330° C , held there for a few hours, and then allowed to cool to room temperature. The composition, as determined by weighing before and after introducing the hydrogen, was 7.558 gram atoms of titanium and 2.563 gram atoms of hydrogen. X-ray powder photographs of the sample showed the presence of both α and γ phases.

Results

Twenty-four heat-capacity measurements were made between approximately 4° and 15° K . The data are given in table II. The heat capacity was again found to obey the relationship $C = \gamma T + \beta T^3$ up to about 13° K ,

and a least-squares procedure gave the equation

$$C = 0.0242T + 2.294 \times 10^{-4}T^3 \text{ joules/deg}$$

A plot of C/T versus T^2 is shown in figure 6.

In order to evaluate tentatively the specific heat of the γ titanium, it will be assumed that the boundary on the phase diagram between the region of homogeneous α and the two-phase region of α plus γ lies at 50 atomic percent. This is approximately the value suggested by Lenning, Craighead, and Jaffee (ref. 2). The present sample then can be considered to consist of essentially pure titanium Ti and the hydride can be considered to have a composition represented by TiH. Since the overall composition of the sample is 25.33 atomic percent hydrogen, the actual quantities of the two phases present are 4.993 gram atoms of titanium and 2.563 moles of TiH. Subtracting the heat capacity of 4.993 gram atoms of Ti from the total heat capacity of the hydride sample gives

$$C = 0.0073T + 0.998 \times 10^{-4}T^3 \text{ joules/deg}$$

Dividing through by the number of moles of TiH leads to

$$C = 0.00285T + 0.389 \times 10^{-4}T^3 \frac{\text{joules}}{\text{deg mole TiH}}$$

This may be compared with the corresponding equation for pure Ti which is

$$C = 0.00338T + 0.260 \times 10^{-4}T^3 \frac{\text{joules}}{\text{deg g atom Ti}}$$

The electronic heat capacity of TiH is only slightly lower than that of pure Ti. Since Ti and TiH belong to different crystal systems, it is impossible at present to ascribe this difference unambiguously to variation in the density of states. The value of θ for TiH computed from these data is 368° K.

Precision

The precision of the measurements on the hydride is represented graphically in figure 7, where the deviation of the measured values of the heat capacity from the values computed from the least-squares equation

is plotted as a function of temperature. The average deviation is 0.56 percent for 21 points below 13° K. This improvement over the precision for the titanium sample arises, at least in part, from an increase in the skill of the operators as they gained experience with the apparatus.

University of Pittsburgh,
Pittsburgh, Pa., August 8, 1955.

APPENDIX

CALCULATION OF EFFECTIVE HEAT CAPACITY
OF HELIUM GAS IN THERMOMETER

The effective heat capacity of helium gas in the thermometer may be calculated as follows:

For an open system

$$dq = nT dS \quad (1)$$

where dS is the change of entropy of a system of n moles of material at the temperature T due to the reversible absorption of a change in quantity of heat dq .

If v is the molar volume of the helium gas ($nv = V$ is the actual volume), the change in entropy can be expressed as

$$dS = \left(\frac{\partial S}{\partial T} \right)_v dT + \left(\frac{\partial S}{\partial v} \right)_T dv \quad (2)$$

Since

$$\left(\frac{\partial S}{\partial T} \right)_v = \frac{C_v}{T}$$

where C_v is the atomic heat of helium gas at constant volume, and

$$\left(\frac{\partial S}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v$$

where P is pressure, equation (2) becomes

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dv \quad (3)$$

Assuming the ideal gas law to be valid, where R is the gas constant,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

and equation (3) becomes

$$dS = \frac{C_V}{T} dT + \frac{nR}{V} dv$$

Substituting this into equation (1) gives

$$dq = nC_V dT + n\left(\frac{nRT}{V}\right)dv$$

or

$$dq = nC_V dT + nP dv \quad (4)$$

From the ideal gas law

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP = \frac{R}{P} dT - \frac{RT}{P^2} dP$$

This transforms equation (4) into

$$dq = nC_V dT + nR dT - V dP \quad (5)$$

Now,

$$dP = \frac{RT}{V} dn + \frac{nR}{V} dT \quad (6)$$

Combining equations (5) and (6) yields

$$dq = nC_V dT - RT dn$$

Applying this equation to the helium gas thermometer gives

$$dq_1 = n_1 C_v dT_1 - RT_1 dn_1 \quad (7)$$

where C_v is the atomic heat of helium gas at constant volume, n_1 is the number of moles of helium in the thermometer bulb, and T_1 is the temperature of the thermometer bulb.

From the preceding equations

$$n_1 = n_o - \frac{P}{R} \left(\sum \frac{V}{T} \right) \quad (8)$$

$$dn_1 = - \frac{1}{R} \left(\sum \frac{V}{T} dP \right) \quad (9)$$

$$T_1 = \frac{PV_1}{Rn_1} = \frac{PV_1}{R \left[n_o - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right]} \quad (10)$$

$$dT_1 = \frac{V_1 n_o}{R \left[n_o - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right]^2} dP \quad (11)$$

$$dP = \frac{R \left[n_o - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right]^2}{V_1 n_o} dT_1 \quad (12)$$

Since the object is to compute the heat capacity of the gas, the term $\sum (V/T)$ now includes all volumes in the thermometer system except the thermometer bulb and one-half of the volume of the tube connecting the sample container and shield.

Combining equations (7), (8), (9), and (11) gives

$$\begin{aligned} dq_1 &= \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right] C_v dT_1 + \frac{RPV_1}{R \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right]} \frac{1}{R} \left(\sum \frac{V}{T} \right) \frac{R \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right]^2}{V_1 n_0} dT_1 \\ &= \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right] C_v dT_1 + \frac{P \left(\sum \frac{V}{T} \right) \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right]}{n_0} dT_1 \end{aligned}$$

The atomic heat of helium at constant volume (see Keesom, ref. 7) is

$$C_v = \frac{3}{2} R - \frac{1}{2} \rho^2 RT \frac{d^2(CT)}{dT^2} \quad (13)$$

where C is the third virial coefficient for helium and ρ is the density in moles per liter. At pressures employed in the present calorimeter the term $\frac{1}{2} \rho^2 RT \frac{d^2(CT)}{dT^2}$ is significant only below about 4.5° K.

Thus, at temperatures between 4.5° and 15.5° K the heat capacity of helium gas is taken as

$$C_n = \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right] \frac{3}{2} R + \frac{P}{n_0} \left(\sum \frac{V}{T} \right) \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right] \quad (14)$$

Below 4.5° K the heat capacity is computed from

$$C_n = \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right] \left[\frac{3}{2} R - \frac{1}{2} \rho^2 RT \frac{d^2(CT)}{dT^2} \right] + \frac{P}{n_0} \left(\sum \frac{V}{T} \right) \left[n_0 - \frac{P}{R} \left(\sum \frac{V}{T} \right) \right] \quad (15)$$

in conjunction with the virial-coefficient data for helium.

REFERENCES

1. Hägg, Gunnar: Röntgenuntersuchungen über die Hydride von Titan Zirkonium Vanadin und Tantal. Zs. phys. Chemie, Abt. B, Bd. 11, 1930-1931, pp. 433-454.
2. Lenning, G. A., Craighead, C. M., and Jaffee, R. I.: Constitution and Mechanical Properties of Titanium-Hydrogen Alloys. Jour. Metals, vol. 6, no. 3, Mar. 1954, pp. 367-376.
3. Clement, J. R., and Quinnell, E. H.: Low Temperature Characteristics of Carbon-Composition Thermometers. Rev. Sci. Instr., vol. 23, no. 5, May 1952, pp. 213-216.
4. Estermann, I., Friedberg, S. A., and Goldman, J. E.: Specific Heats of Several Metals Between 1.8° and 4.2° K. Phys. Rev., vol. 87, no. 4, Aug. 15, 1952, pp. 582-588.
5. Morrison, J. A., Patterson, D., and Dugdale, J. S.: An Adiabatic Calorimeter for the Temperature Region Below 20°K. - The Specific Heat of Sodium Chloride. Can. Jour. Chem., vol. 33, no. 2, Feb. 1955, pp. 375-382.
6. Garfunkel, M. P., and Wexler, A.: Measurements of High Vacuums at Low Temperatures. Rev. Sci. Instr., vol. 25, no. 2, Feb. 1954, pp. 170-172.
7. Keesom, Willem Hendrik: Helium. Elsevier Pub. Co., 1942, p. 49.
8. Kothen, Charles W., and Johnston, Herrick L.: Low Temperature Heat Capacity of Inorganic Solids. XVII. Heat Capacity of Titanium From 15 to 305° K. Jour. Am. Chem. Soc., vol. 75, no. 13, July 5, 1953, pp. 3101-3102.

TABLE I

MEASURED HEAT CAPACITY OF TITANIUM

T, °K	C, $\frac{\text{joules}}{\text{deg g atom}}$
5.686	2.30×10^{-2}
6.316	2.75
6.986	3.16
7.640	3.70
8.288	4.26
8.953	4.98
9.621	5.71
10.319	6.12
11.042	7.15
11.693	8.17
12.336	9.20
12.978	9.87
13.619	10.68
14.233	12.4
14.899	14.0
15.555	15.5
3.946	1.45
4.450	1.71
4.917	1.98
5.381	2.19
5.867	2.56
11.691	7.98
12.344	8.98
12.998	10.17
13.648	10.92
14.287	12.6
6.348	2.90
6.984	3.28
7.618	3.87
8.253	4.36
8.898	4.90
9.559	5.54
10.242	6.33
15.129	15.3
15.757	16.7

TABLE II

HEAT CAPACITY OF HYDRIDE SAMPLES CONTAINING
7.558 GRAM ATOMS TI + 2.563 GRAM ATOMS H

T, °K	C, $\frac{\text{joules}}{\text{deg}}$
4.837	0.143
5.406	.168
5.931	.189
6.457	.214
6.993	.247
7.537	.281
8.097	.323
8.665	.364
9.229	.404
9.787	.452
10.349	.505
10.914	.559
11.484	.624
12.049	.690
12.614	.762
13.180	.849
13.749	.928
14.322	1.023
14.893	1.142
15.457	1.235
16.021	1.371
16.590	1.504
17.157	1.649
17.722	1.798
3.895	.983
4.427	.129
4.990	.150
5.459	.169
5.959	.191
6.513	.221
16.672	1.552
17.236	1.717
17.802	1.841

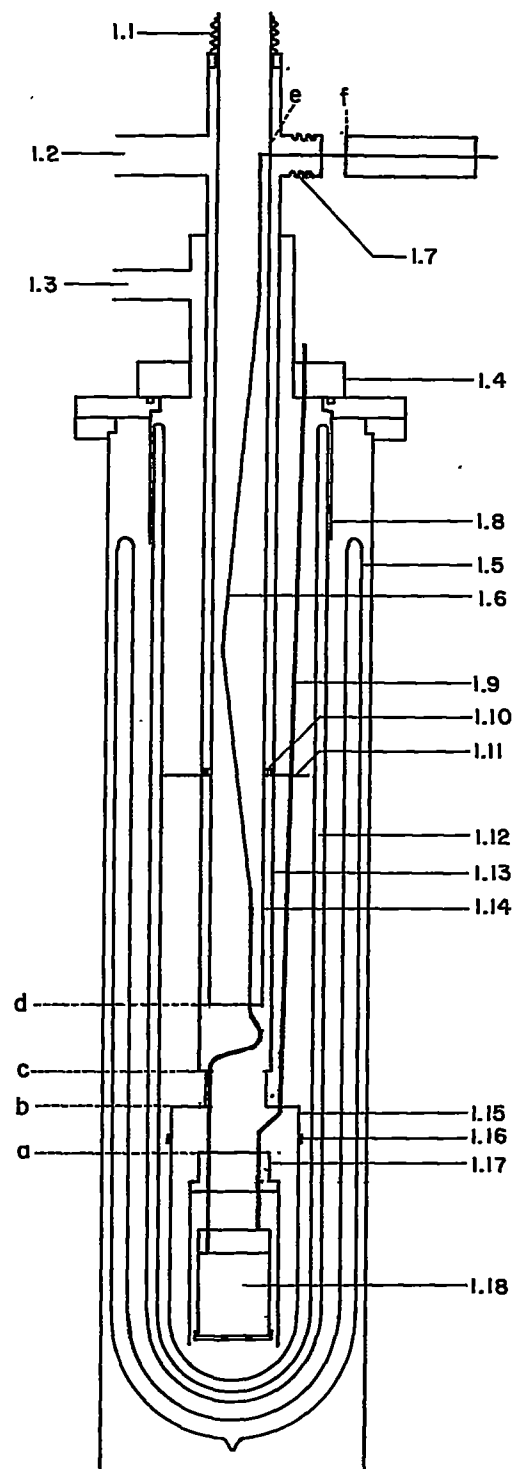


Figure 1.- Calorimeter assembly.

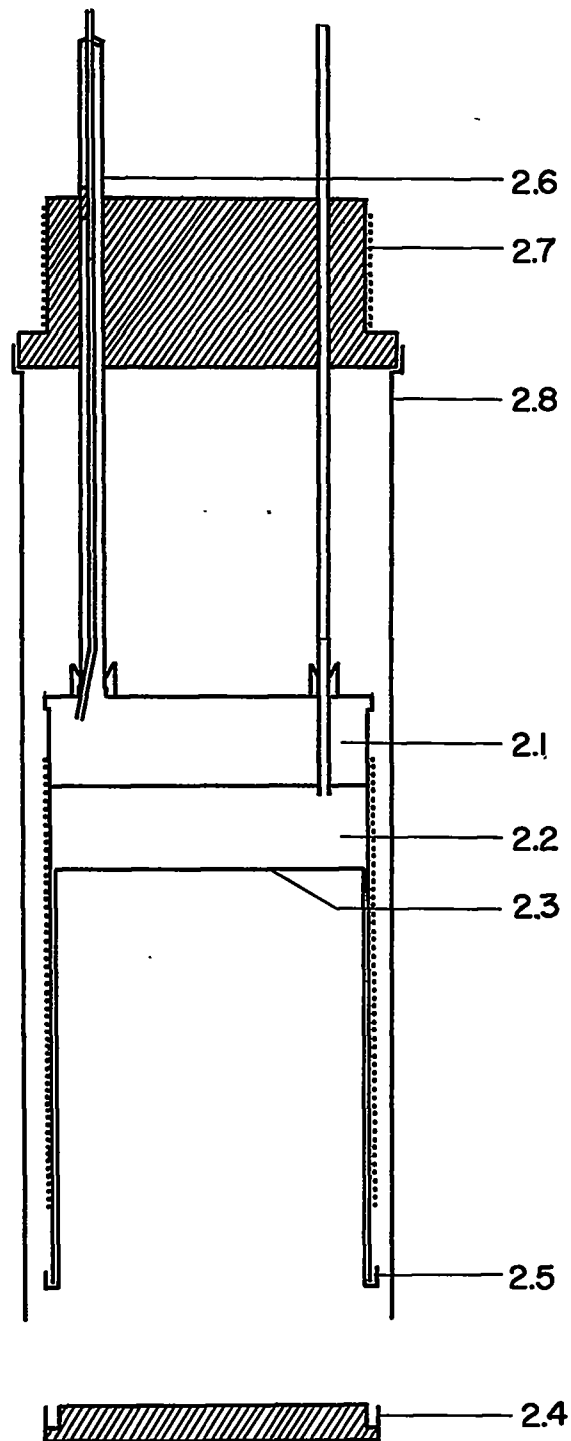


Figure 2.- Sample container.

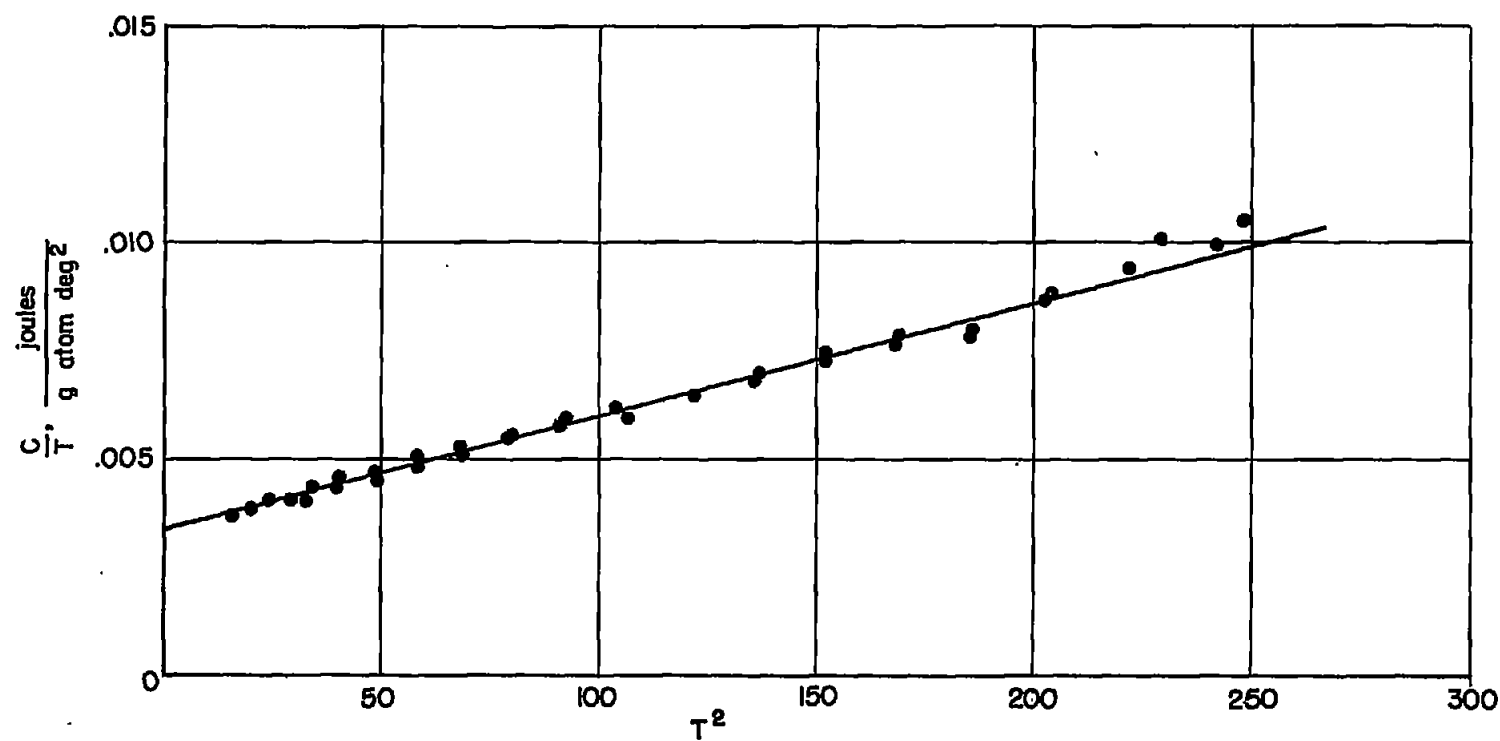


Figure 4.- Plot of C/T versus T^2 for titanium. Equation for straight line is $C/T = 3.38 \times 10^{-3} + 2.596 \times 10^{-5}T^2$ joules/g atom deg².

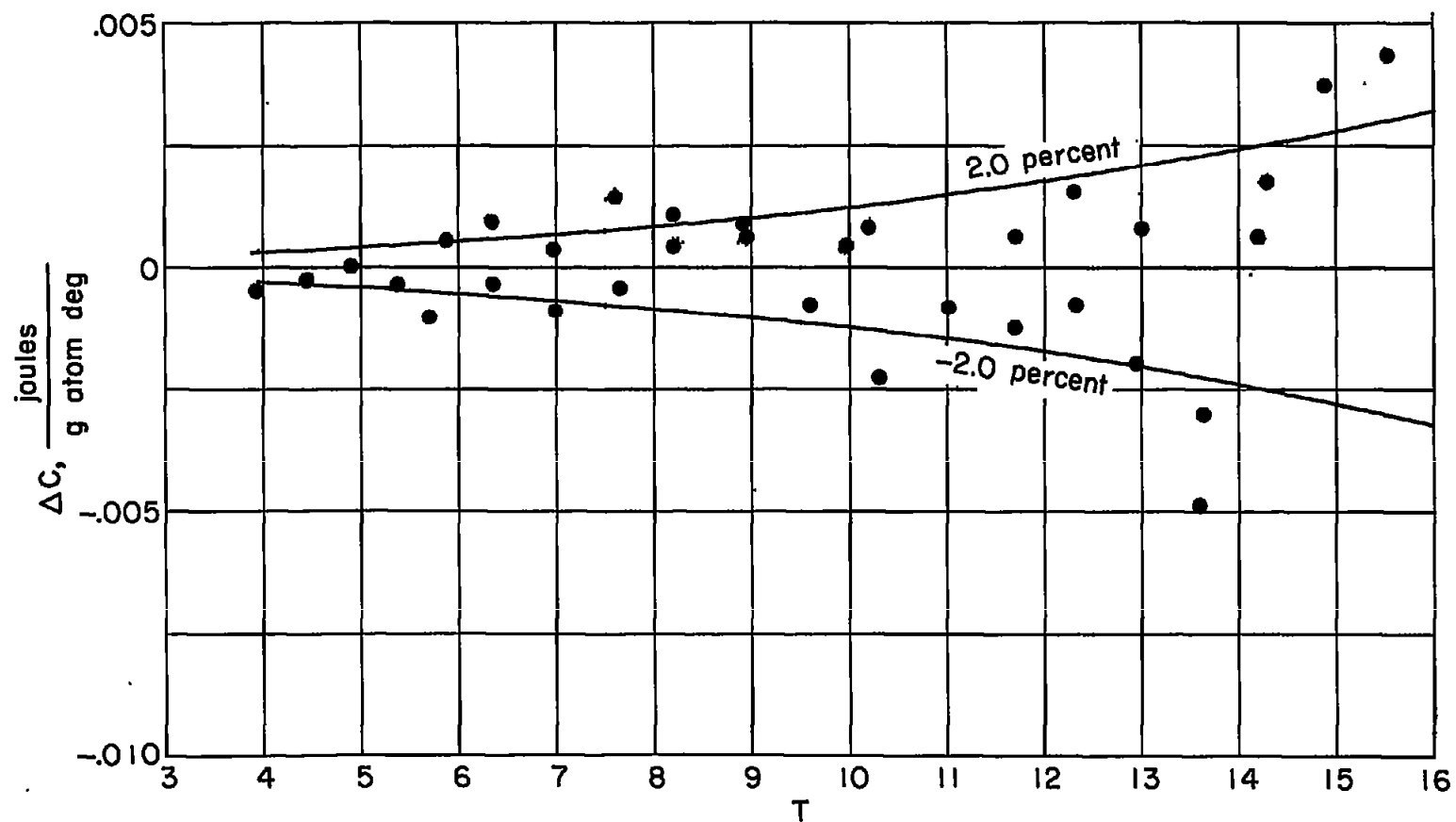


Figure 5.- Deviation of measured atomic heat values of titanium from values calculated by equation $C = 3.38 \times 10^{-3}T + 2.596 \times 10^{-5}T^3$ joules/g atom deg.

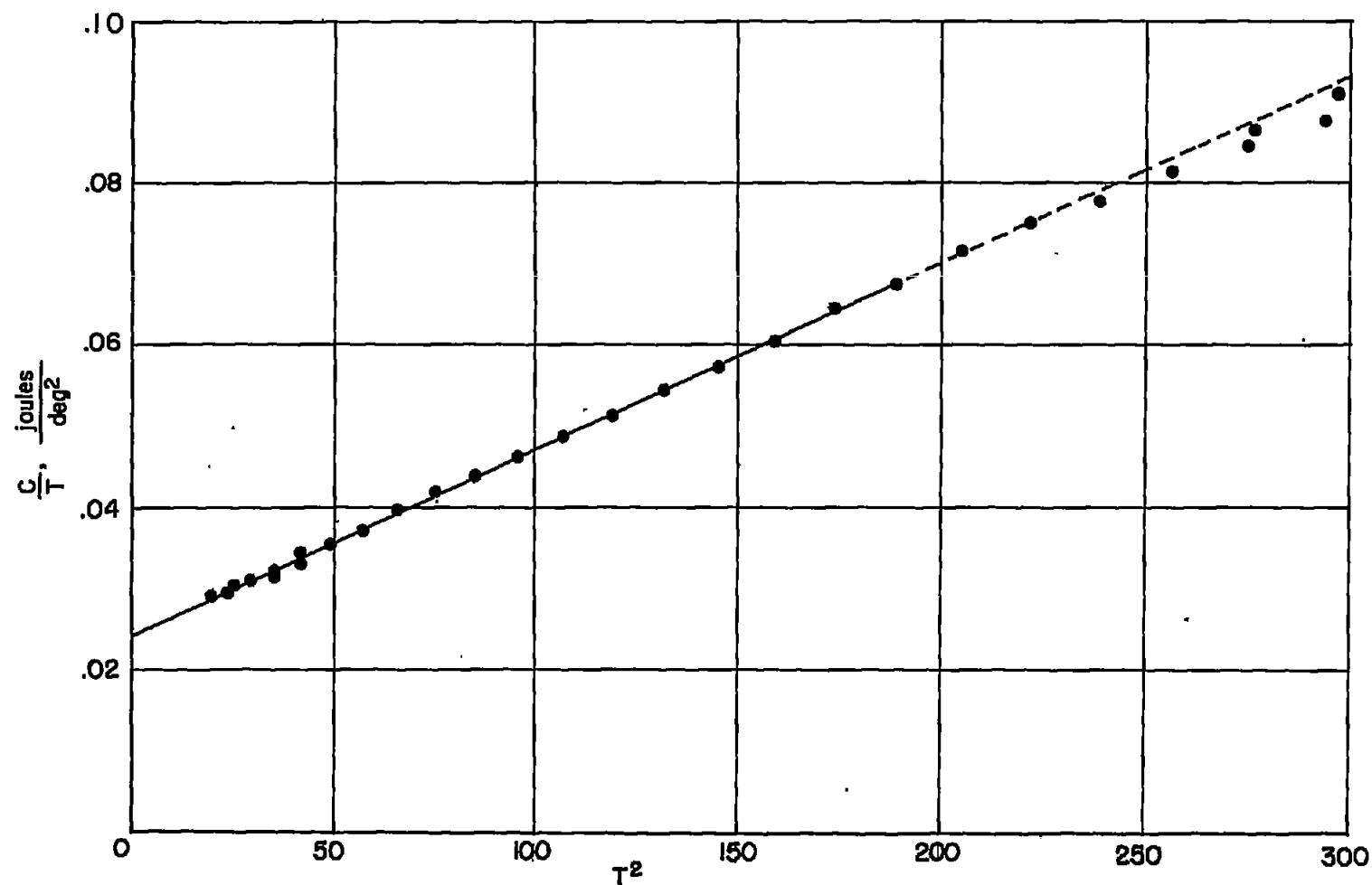


Figure 6.- Plot of C/T versus T^2 for sample containing 7.5556 gram atoms Ti and 2.563 gram atoms H. Equation for straight line is $C/T = 0.0242 + 2.294 \times 10^{-4}T^2$ joules/deg².

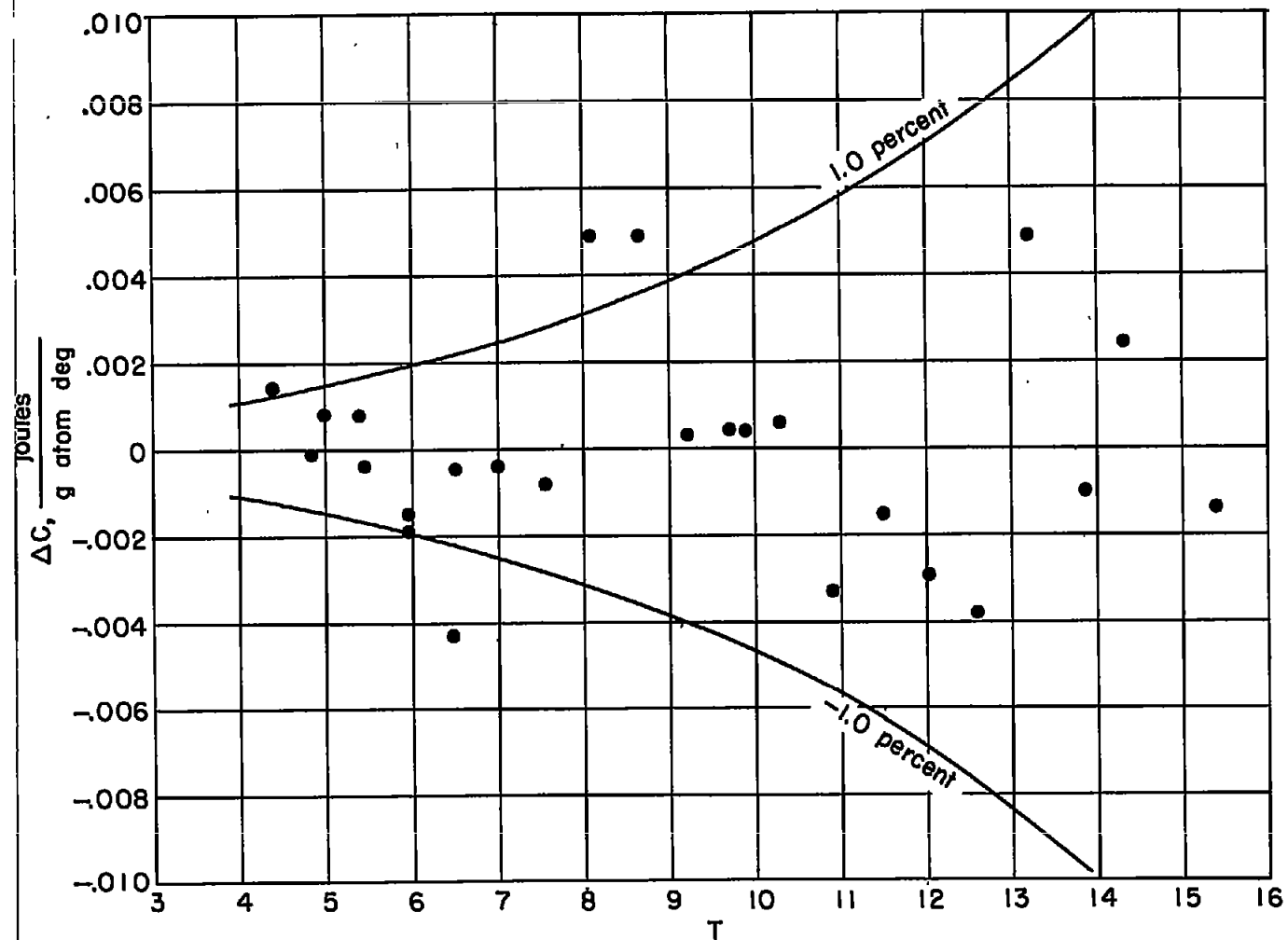


Figure 7.- Deviation of measured heat-capacity values of titanium-hydride sample from values calculated by equation $C = 0.0242T + 2.294 \times 10^{-4}T^3$ joules/deg.

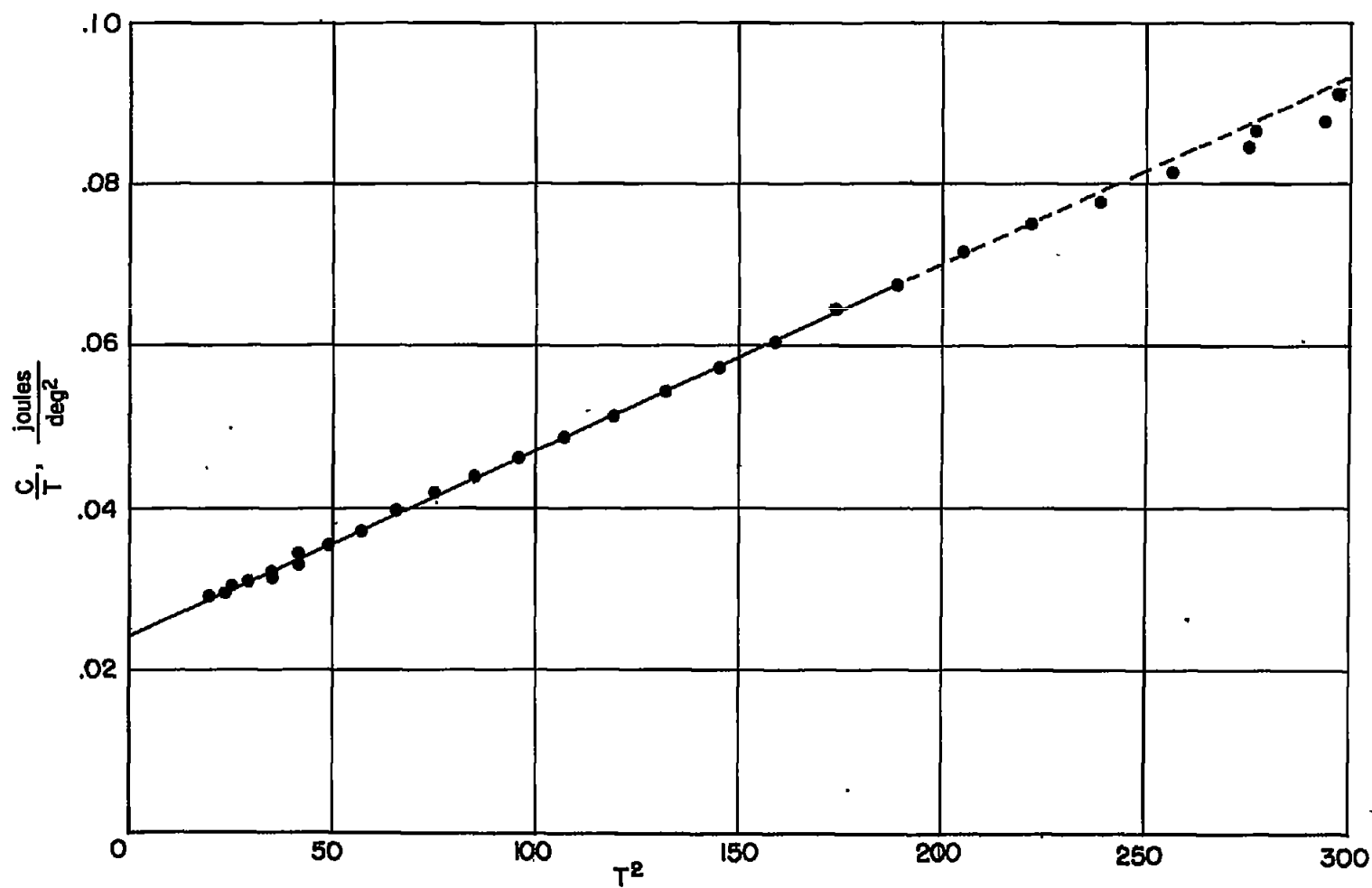


Figure 6.- Plot of C/T versus T^2 for sample containing 7.5556 gram atoms Ti and 2.563 gram atoms H. Equation for straight line is $C/T = 0.0242 + 2.294 \times 10^{-4}T^2$ joules/deg².

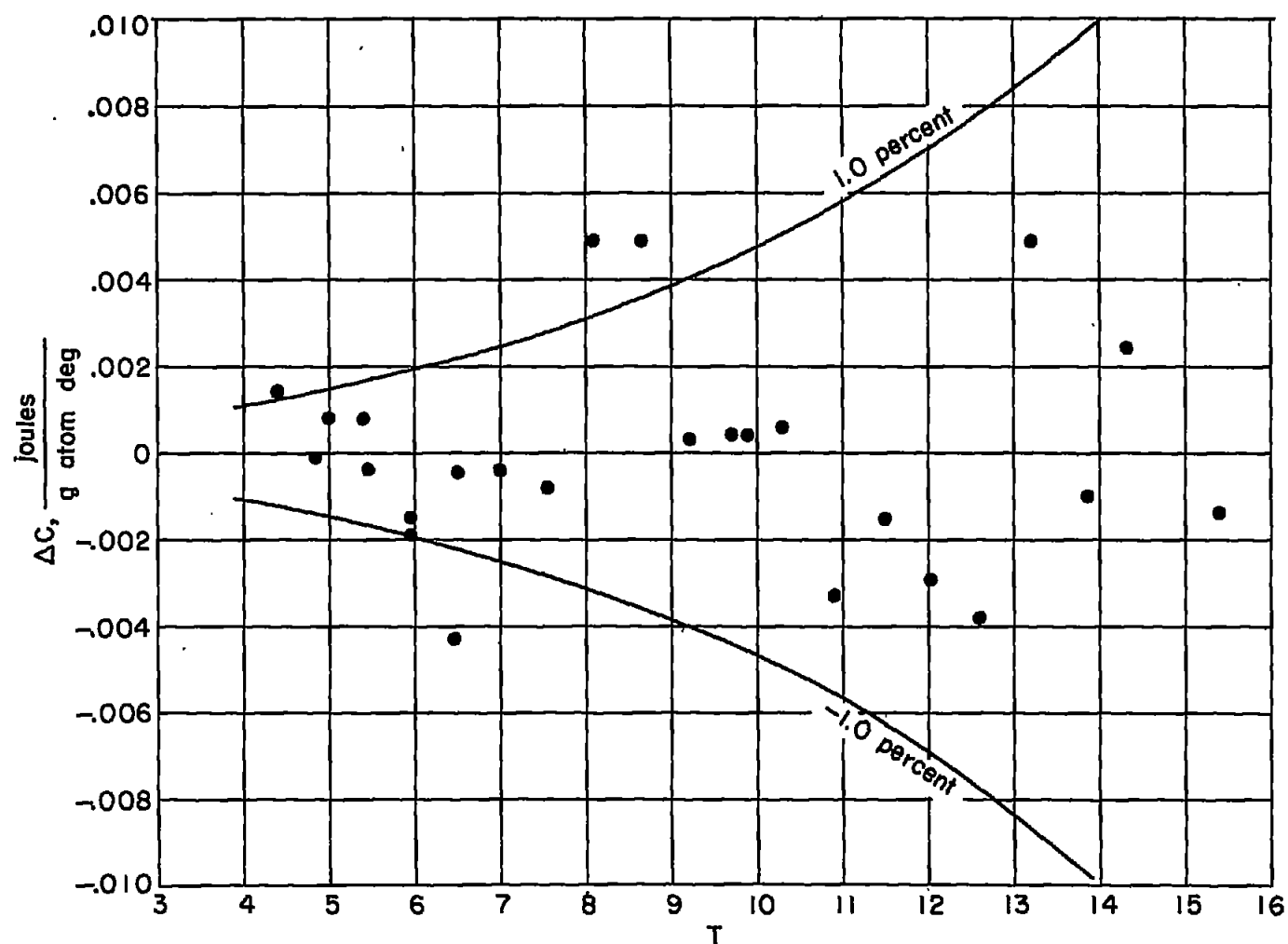


Figure 7.- Deviation of measured heat-capacity values of titanium-hydride sample from values calculated by equation $C = 0.0242T + 2.294 \times 10^{-4}T^3$ joules/deg.